

Research Article

Oxidation of Aromatic Anils by Potassium Peroxymonosulfate in Acetonitrile Medium

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Abstract

The oxidation of aromatic anils by potassium peroxydisulfate is investigated in acetonitrile medium. The reaction followed first order kinetics with respect to the concentration of [anil] and is the first order with respect to potassium peroxydisulfate. The increase of H^+ in this oxidation retards the rate of the reaction. The added $Mn(II)$ decreases the rate of the reaction, which indicates the involvement of two-electron transfer. Correlation of the experimental data of solvent reveals that solvent interaction plays a major role in leading the reactivity and a suitable mechanism is proposed.

Keywords: aromatic anils, oxidation, potassium peroxydisulfate, acetonitrile.

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Introduction

Potassium peroxydisulfate (PPDS), an efficient oxidant, has found in organic synthesis due to its versatility, stability, the nontoxic nature, and inexpensive [1]. Potassium salt of peroxodisulphuric acid (PPDS) is obtained as a mixture of $KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$. Aromatic anils, $X-CH=N-Y$ have two phenyl rings X and Y, the ring X- originates from the aromatic benzaldehyde moiety and Y from aniline moiety. The kinetics and mechanism of oxidation of some substituted aromatic anils, using several oxidants have been reported [2-16]. Herein, I would like to report the oxidation of aromatic anils using PPDS in aqueous acetonitrile medium.

Experimental

Anils are prepared [12-17] by refluxing equimolar quantities of benzaldehyde and aniline in ethanol for about 2 to 3 h. The resulting solution is cooled and poured into cold water. The precipitated anil is filtered off, washed with ethanol and dried. It is recrystallised from ethanol. All the reagents are prepared just before the reactions are carried out. Aqueous solution of potassium peroxydisulfate (Sigma Aldrich) is prepared fresh and standardized iodometrically. All the reactions are carried out in a thermostat and the temperature is controlled to $\pm 0.1^\circ C$. The reactions are performed under pseudo-first order conditions by maintaining excess of anil over oxidant. The mixture is homogeneous throughout the course of the reaction.

The progress of the reactions is followed by estimating the unreacted oxidant iodometrically at regular time intervals. The rate constants (k_{obs}) are from log (titre) versus time plots. All the rate constants are averages of two or more determinations. Under kinetic conditions, stoichiometric amounts of the substrate and potassium peroxydisulfate are mixed. The reaction mixture ethanol is extracted. The dark brown extract, when subjected to TLC, gives two distinct spots. On evaporation of ethanol the products are found to be benzaldehyde which is identified by the isolation of its 2,4-dinitrophenylhydrazone derivative and azobenzene identified by its m. p. and UV-VIS spectrum.

The oxidation reactions of meta- and para- substituents of aromatic anils are studied at different temperatures (298, 303, 308, 313 and 318K) to evaluate various thermodynamic parameters. From the Eyrings equation, [18] the thermodynamic parameters, enthalpy of activation and entropy of activation are figured out from the expression

$$k_{obs} = (k_b T / h) \exp^{\Delta G^\ddagger / RT}$$

Where k_b is Boltzmann's constant, T is the temperature in Kelvin, h is plank's constant, R is the gas constant, ΔG^\ddagger is the activation of Gibbs free energy, ΔH^\ddagger is the enthalpy of activation and ΔS^\ddagger is the entropy of activation. ΔG^\ddagger and energy of activation (E_a) can be calculated from the following expressions respectively.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S \quad \text{and} \quad E_a = \Delta H^\ddagger + RT$$

Results and Discussion

The reaction followed first order kinetics with respect to the concentration of anil and is the first order with respect to the concentration of PPMS. Under the identical experimental conditions $[\text{Anil}] \gg [\text{PPMS}]$, the pseudo-first order linear plot of $\log(\text{titre})$ versus time is linear upto 80%, depicted in **Figure 1**.

The order in $[\text{anil}]$ is the first, as revealed by the slope of the plot of $\log k_{\text{obs}}$ against $\log [\text{Anil}]$ (**Figure 2**), with correlation coefficient ($r = 0.998$).

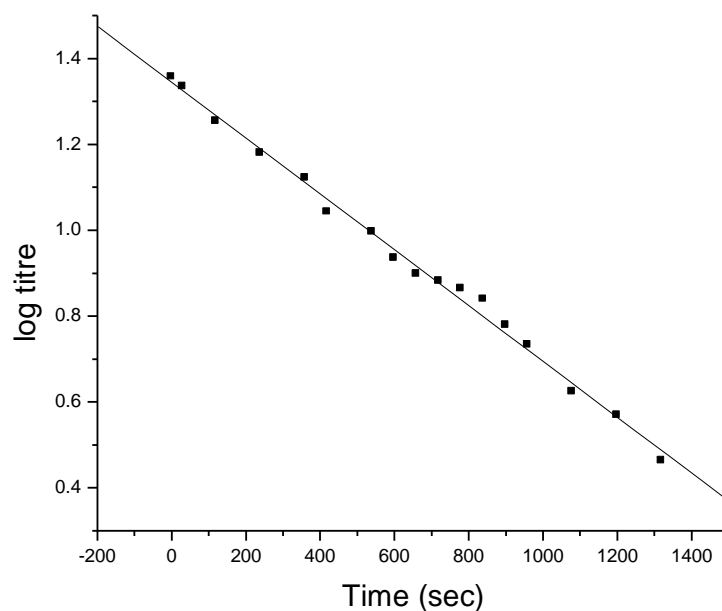


Figure 1 Pseudo-first order plot for PPMS oxidation of aromatic anil at 308 K.

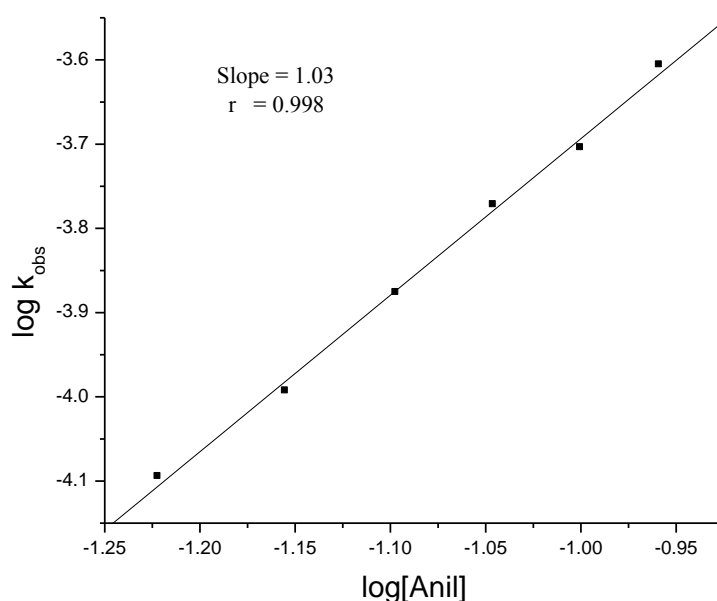


Figure 2 Plot of $\log [\text{Anil}]$ vs $\log k_{\text{obs}}$ at 308K.

The kinetic order in acidity appears to be united, but increase in $[H^+]$, decreases the rate of the reaction. The kinetic results are summarized in **Table 1**. The ionic strength of the reaction varies by the addition of Na_2SO_4 and its influence on reaction rate is studied and it is found that it has no significant effect on the reactivity. Addition of $Mn(II)$ decreases the rate of the reaction and the rate data are listed in **Table 2**. Temperature dependence studies are conducted for all the substituted anils between 298 and 318 K. The rate constants for the reaction systems and activation parameters are evaluated from the Eyring plots as listed in **Table 3**.

Table 1 Effect of varying the concentration of Anil, PPMS, H_2SO_4 and solvent composition on the rate at 308K.

10^2 [Anil] (mol dm ⁻³)	10^3 [PPMS] (mol dm ⁻³)	$[H^+]$ (mol dm ⁻³)	CH ₃ CN (%)	10^4 k _{obs} (s ⁻¹)
5.0	5.0	1.0	50	3.61
6.0	5.0	1.0	50	4.52
7.0	5.0	1.0	50	4.90
8.0	5.0	1.0	50	5.81
9.0	5.0	1.0	50	6.53
7.0	4.0	1.0	50	4.77
7.0	5.0	1.0	50	4.91
7.0	6.0	1.0	50	4.82
7.0	7.0	1.0	50	4.94
7.0	8.0	1.0	50	4.75
7.0	5.0	0.8	50	6.27
7.0	5.0	0.9	50	5.65
7.0	5.0	1.0	50	4.92
7.0	5.0	1.1	50	4.46
7.0	5.0	1.2	50	4.04
7.0	5.0	1.0	30	5.62
7.0	5.0	1.0	40	4.85
7.0	5.0	1.0	50	4.53
7.0	5.0	1.0	60	4.32
7.0	5.0	1.0	70	3.94

[Anil] = 0.1 mol dm⁻³; [PPMS] = 0.005 mol dm⁻³; [H_2SO_4] = 1.0 mol dm⁻³; CH₃CN – H₂O = 60%-40% (v/v); Temperature = 308 K

Table 2 Effect of [Mn(II)], [acrylonitrile], [Na_2SO_4] on the reaction rate at 308 K.

[Mn(II)] (mol dm ⁻³)	[Acrylonitrile] (mol dm ⁻³)	[Na_2SO_4] (mol dm ⁻³)	10^4 k _{obs} (s ⁻¹)
0	-	-	7.45
0.02	-	-	7.12
0.04	-	-	6.27
0.06	-	-	5.37
0.08	-	-	4.40
-	0	-	4.56
-	0.02	-	5.02
-	0.04	-	5.07
-	0.06	-	4.79
-	0.08	-	4.35
-	-	0	4.72
-	-	0.02	5.19
-	-	0.04	5.35
-	-	0.06	5.13
-	-	0.08	5.24

[Anil] = 0.08 mol dm⁻³; [PPMS] = 0.005 mol dm⁻³; [H_2SO_4] = 1.0 mol dm⁻³; CH₃CN – H₂O = 60%-40% (v/v); Temperature = 308 K

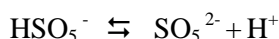
Table 3 Temperature effect and thermodynamic parameters of PPMS oxidation of anils.

S. No.	Substituents	$10^{-4} \times k_{\text{obs}} (\text{s}^{-1})$					ΔH^\ddagger	$-\Delta S^\ddagger$	ΔG^\ddagger	E_a	R	SD
		25°C	30°C	35°C	40°C	45°C	kJ mol^{-1}	$\text{J K}^{-1} \text{mol}^{-1}$	kJ mol^{-1}	$\text{kJ mol}^{-1} \text{K}^{-1}$		
1	H	4.65	5.58	6.47	7.05	9.46	23.43	229.11	94.17	25.72	0.987	0.07
2	m-CH ₃	3.13	3.32	4.23	5.11	8.28	33.35	200.25	95.06	35.66	0.972	0.16
3	p-CH ₃	4.21	4.16	4.41	4.78	5.60	8.12	282.47	95.32	10.29	0.889	0.07
4	p-OC ₂ H ₅	3.29	3.58	3.39	6.13	7.34	29.21	213.13	95.48	31.57	0.976	0.15
5	p-OCH ₃	3.06	3.20	4.05	4.26	6.15	24.38	230.62	95.31	26.42	0.995	0.05
6	p-Cl	4.28	5.71	7.12	7.49	20.27	49.63	142.57	93.65	52.15	0.937	0.17
7	m-Cl	4.37	5.04	5.68	7.11	12.23	34.36	194.18	94.17	36.71	0.966	0.12
8	m-NO ₂	6.09	6.17	8.23	9.23	11.09	21.37	234.22	93.64	23.58	0.997	0.05
9	p-NO ₂	3.52	5.17	5.54	14.17	22.21	69.26	78.02	93.36	72.16	0.978	0.27

[Anil] = 0.1 mol dm⁻³; [PPMS] = 0.005 mol dm⁻³; [H₂SO₄] = 1.0 mol dm⁻³; CH₃CN – H₂O = 60%-40% (v/v)

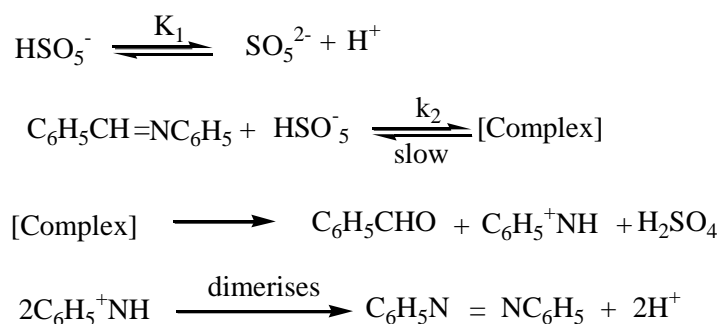
Mechanism

The addition of acrylonitrile monomer shows no variation in the reaction rate and no formation of polymer in the oxidation of aromatic anils [12-16]. This rules out the presence of free radical mechanism in this oxidation reaction. So the ionic reaction is preferred in this oxidation study. Generally, the enhancement of the electrophilic activity of peroxide will minimize the significance of undesirable free radical methods, resulting in a mixture of products. Literature study [19] reveals that at higher pH, the PMS exists as dianion ($\text{O}^{\ominus}\text{O}-\text{O}_3^{\ominus}$) and at lower pH, the oxidant exists as HSO_5^{\ominus} ions. The absorption spectra represent spectral changes supporting the complex formation. The investigation results illustrate a fascinating note that the increase of H^+ retards the rate of the reaction. With the decrease of pH, the molecule gains a proton, becomes less negatively charged and hence the rate of the reaction decreases [20].



The species HSO_5^- is more reactive than SO_5^{2-} species. The higher reactivity of HSO_5^- is consistent both with an electrostatic effect and with weakening of the peroxide bond by the proton [21]. Also in strong acid, the anil exists as $\text{C}_6\text{H}_5\text{CH}=\text{NHC}_6\text{H}_5^+$ form. It is observed that when the acid strength is increased, there is a decrease in the rate which may be due to the less reactive protonated form than non-protonated form.

Based on the stoichiometry of the reaction and above experimental results, the following reactions (**scheme 1**) are believed to constitute the most probable mechanism of the reaction. The formation of complex is in agreement with the literature study [7, 22] and the intermediate formed is experimentally confirmed at 790nm.

**Scheme 1** Probable mechanism for the oxidation of aromatic anil by PPMS

The next step (decomposition of complex) is a slow reaction and is likely to be the rate determining step. Simultaneously, at 429nm, a peak appears and is stable till the end of the reaction, which is the azobenzene product. Based on the above experimental observations, a probable mechanism, shown in Scheme 1 is suggested.

The above mechanism leads to the following rate law:

$$\text{Rate} = -d[\text{KHSO}_5] / dt = K_1 k_2 [\text{anil}] [\text{KHSO}_5]$$

This rate law satisfactory explains all the experimental results.

Eyring's Plot for PPMS Oxidation of Anils

The effect of substituents on the rate is studied by varying the substituents H, m-CH₃, p-CH₃, p-OC₂H₅, p-OCH₃, p-Cl, m-Cl, m-NO₂ and p-NO₂ in one of the rings aniline at five different temperatures 298, 303, 308, 313 and 318K (Table 3), ΔH^\ddagger and ΔS^\ddagger values are calculated from the slope and intercept of the plot $\ln k_{\text{obs}}/T$ versus $1/T$, respectively (Figure 3). The analysis of the data in the Table 3 indicates that the oxidation is neither isoenthalpic nor isoentropic but confirms with isokinetic relationship of compensation law.

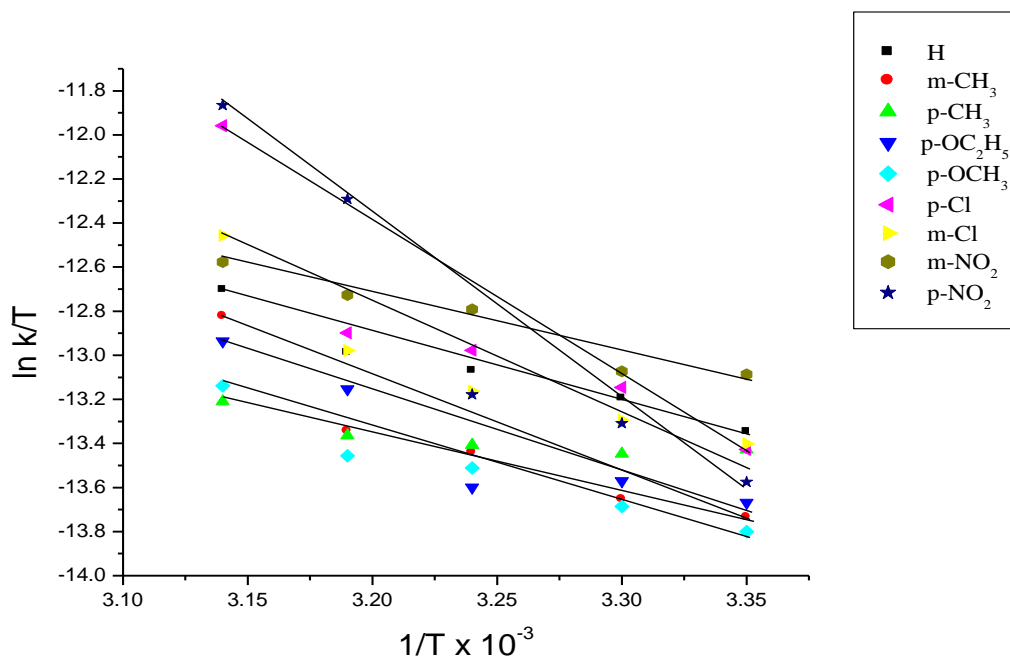


Figure 3 Eyring's plot for PPMS oxidation of anils at 308K.

Conclusion

The oxidation of aromatic anils by PPMS is the first order with respect to [anil] and is the first order with respect to PPMS and is the first order with respect to [acid] under the experimental conditions, and the aromatic anil is oxidized to benzaldehyde and azobenzene. Correlation of the experimental data of solvent reveals that solvent interaction plays a major role in leading the reactivity. The isokinetic plot and Exner plot reveal that there is no change in reaction mechanism with respect to substituents in aromatic anils. The formation of charged intermediate compound was supported by the high negative values of entropy of activation and a most probable mechanism has been proposed for oxidation of anils by PPMS.

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